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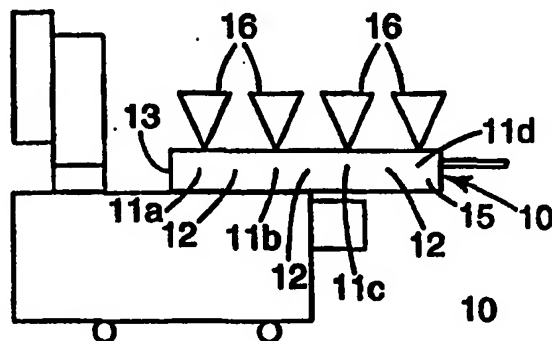
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B29C 47/10, 43/18, 45/14, A61G 7/057		A1	(11) International Publication Number: WO 97/00163
			(43) International Publication Date: 3 January 1997 (03.01.97)
(21) International Application Number: PCT/US96/06855		(81) Designated States: AU, CA, JP, KR, SG, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(22) International Filing Date: 14 May 1996 (14.05.96)			
(30) Priority Data: 60/000,229 15 June 1995 (15.06.95) US		Published <i>With international search report.</i>	
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(54) Title: **METHOD FOR MANUFACTURING SOLID ELASTOMERIC GELS**

(57) Abstract

Solid elastomeric gel is produced in a continuous process using a twin screw extruder (10). Gel from the extruder (10) can be fed through a die (21) to form a length of the gel (20) with a uniform cross section and then cut to length to provide pieces of the gel (20) for use in a pad. Alternatively, gel from the extruder (10) may be injected into a chamber between a rigid base portion and a thermoplastic sheet to form that sheet and a surface of the layer of gel in the cavity against a surface in a cavity, thereby producing a pad including the layer of gel that has a precise predetermined peripheral shape corresponding to the surface in the cavity and is covered by the sheet which also has that peripheral shape and is wrinkle free.



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METHOD FOR MANUFACTURING SOLID ELASTOMERIC GELS

5. Field of the Invention

The present invention relates to the manufacture of solid elastomeric gels and to the formation of pads including layers of such gels.

Background

10 Pads including layers of solid elastomeric gels such as those described in U.S. Patent No. 3,676,387 have been proven to be highly effective in reducing the affect of pressure points on portions of a person supported on the pads, thereby reducing tissue inflammation (e.g., "bed sores") and loss of circulation to extremities due to restriction of blood flow.

15 U.S. Patent Applications Nos. 08/253,510 filed June 3, 1994, and 08/324,734 filed October 18, 1994, describe wrist rests adapted to be used by a computer operator which include covered layers of solid elastomeric gel on which the wrists of the computer operator may be supported. The layers of solid elastomeric gel in those pads retain their shape and provide a conformable contour
20 that distributes the weight of a users hands and/or forearms across a broad surface area.

Heretofore, the solid elastomeric gels used in such pads have been made in batch processes and subsequently molded to a desired shape. U.S. Patent No. 3,676,387 describes batch processes for making several gel constructions, each of
25 which processes includes placing a polymer and a plasticizer such a mineral oil in a heated vessel, mixing the polymer and plasticizer under medium to high shear for a determined time, and then emptying the vessel. Such batch processes typically require long mixing times and can cause mechanical degradation due to agitation and or can thermal degradation of the polymers due to oxidation. Stabilizers may
30 be added to reduce thermal degradation, but they are limited in their effectiveness and add cost to the process.

Disclosure of the Invention

The present invention provides a method for making solid elastomeric gels more quickly and with less mechanical and thermal degradation than is possible with the batch process described above; together with improved methods for forming
5 pads that include layers of solid elastomeric gel.

Generally, the method according to the present invention is for making solid elastomeric gel from copolymer and plasticizer and includes the steps of (1) providing an extruder having multiple infeed sections each followed by a mixing section along a barrel of the extruder; (2) introducing the copolymer into one of the
10 infeed sections of the operating extruder, (3) heating and shearing the copolymer in a subsequent mixing section, (4) introducing the plasticizer to the copolymer through at least one of the feeding sections in a pattern and at a rate that produces solid elastomeric gel at room temperature that will retain its shape after repeated compression and decompression of the gel, and (5) ejecting the gel from the
15 extruder.

The ejecting step may include ejecting the gel through a die to form a length of the gel having a predetermined cross section, and the method may further include
(6) cutting the extruded gel into lengths to form pieces of the gel with uniform cross sections that can be used in pads.

20 Alternatively, the method can further include the steps of (6) providing a die having a cavity defined by a cavity surface with a predetermined shape and a support surface around the periphery of the cavity; (7) forming a preliminary structure including (a) a rigid base portion adapted to engage the support surface of the die, that has inner and outer surfaces and an inlet passageway communicating
25 between those surfaces; and (b) a thermoplastic sheet having a periphery attached to the periphery of the base portion with the sheet extending over its inner surface to define a chamber between the thermoplastic sheet and the inner surface of the base portion, which chamber has a volume less than the volume of the cavity; and (8)
positioning the base portion against the support surface of the die with the
30 thermoplastic sheet positioned in the cavity at a position spaced from the cavity surface. The ejecting step may then include ejecting the gel through the inlet

passageway into the chamber to thermally deform the sheet into intimate engagement against the cavity surface and to form, when the gel has cooled, a pad including a piece of solid elastomeric gel having a surface covered by the polymeric sheet that corresponds in shape to the cavity surface.

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Brief Description of the Drawing

The present invention will be further described with reference to the accompanying drawing wherein like reference numerals refer to like parts in the several views, and wherein:

10 Figure 1 is a schematic view of an extruder used in the method according to the present invention;

Figure 2 is an enlarged fragmentary view of portions of the screws from the extruder illustrated in Figure 1;

Figure 3 is a sectional view taken approximately along line 3-3 of Figure 2;

15 Figure 4 is a sectional view taken approximately along line 4-4 of Figure 2;

Figure 5 is a schematic view illustrating a first modification of the method illustrated in Figure 1;

Figure 6 is an enlarged sectional view of a die used in the method modification illustrated in Figure 5;

20 Figure 7 is an enlarged perspective view of a piece of solid elastomeric gel made using the method modification illustrated in Figure 5;

Figures 8 and 9 are sectional views illustrating a second modification of the method illustrated in Figure 1; and

25 Figure 10 is a perspective view of a pad made using the second method modification illustrated in Figures 8 and 9.

Detailed Description

Referring now to Figures 1 through 4 there is illustrated a method according to the present invention for making solid elastomeric gel from copolymer and plasticizer. Generally, that method includes the steps of (1) providing a twin screw extruder 10 (e.g., a Werner Pfleiderer Model ZSK 30 twin screw co-rotating

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extruder) that has multiple infeed sections 11a, 11b, 11c and 11d into which material may be fed through hoppers 16, each of which infeed sections 11a, 11b, 11c and 11d is followed by a mixing section 12 along a barrel 13 of the extruder; (2) introducing the copolymer into one of the infeed sections (e.g., 11a) of the extruder 10, (3) heating and shearing the copolymer in a subsequent mixing section 12; (3) introducing the plasticizer to the copolymer through at least one of the infeed sections 11b, 11c and 11d in a pattern and at a rate to produce solid elastomeric gel that at room temperature that will retain its shape after repeated compression and decompression cycles of the gel; and (4) ejecting the solid elastomeric gel from the extruder 10.

Figure 2 illustrates portions of twin screws 14 in the extruder 10 at two of the infeed and mixing sections 11a, 11b, and 12 of the twin screw extruder 10. Figures 3 and 4 illustrate the cross sectional shapes of the twin screws 14 at the mixing and infeed sections respectively. While the specific pitch and type of mixing and infeed sections used is not critical, those sections should be selected to provide sufficient residence time in the various sections to accomplish homogeneous mixing and plasticizing of the copolymer.

The polymer is introduced into the first infeed section 11a of the barrel 13, and is then heated to between 200 and 350 degrees Fahrenheit in the following short mixing section 12. Plasticizer is introduced at the second infeed section 11b and is then heated to a temperature in the range of 200 to 350 degrees Fahrenheit in the next mixing section 12. The mixture then passes through another mixing section 11c heated to a temperature in the range of 250 to 350 degrees Fahrenheit. The barrel 13 and the screws 14 may include any number of infeed and mixing sections 11 and 12 needed to achieve the desired softness for the solid elastomeric gel. After the final mixing section 11, the mixed gel is passed through a cooling feed section 15 to reduce the temperature, and thereby increase the viscosity of the molten gel so that it can be fed either (1) into a storage container (not shown) for later processing, or (2) through a profile extrusion die 21 as will be explained below with reference to Figures 5 through 7, or (3) into an injection mold or die 30 as will

also be explained below, with reference to Figures 8 through 10, or (4) into a form-fill-seal device to fill a flexible sleeve with the gel to form a pad of a desired shape.

Figures 5 through 7 illustrate a first modification of the method illustrated in Figures 1 through 4 that can be used to make pieces 20 of the solid elastomeric gel with uniform cross sections (see Figure 7) that can be used in pads. To make such pieces 20 of solid elastomeric gel, the molten gel from the extruder 10 is pushed through a profile extrusion die 21 onto a conveyor 25 where the at least partially cooled and solidified gel extruded through the die 21 is cut into lengths by a cutting device 22 to form the pieces 20 of the gel with uniform cross sections that can be used in pads.

Figure 6 illustrates details of the profile extrusion die 21 which has an inlet port 23 into which molten gel is fed from the extruder 10 at a temperature and rate that allows the periphery of the gel to conform to the shape of an outlet orifice 24 of the die 21 and, upon being exposed to room temperature air, to solidify to an extent that its peripheral shape in cross section is retained upon further cooling. The profile extrusion die 21 includes a central temperature control section having openings 27 through which heated or cooled liquids or air may circulated or electric heaters may be positioned to help provide temperature control for the gel passing through the die 21.

While Figure 5 illustrates feeding molten gel directly from the extruder 10 into the profile extrusion die 21, solid elastomeric gel made using the extruder 10 or by a batch process at an earlier time may be made molten and fed through the profile extrusion die 21 using means other than the extruder 10, such as a melt pump (not shown).

Figures 8 through 10 illustrate a second modification of the method illustrated in Figures 1 through 4 that can be used to make pads including pieces 28 of the solid elastomeric gel with precise predetermined peripheral shapes. That method further includes the steps of providing the die 30 (Figures 8 and 9) having a cavity defined by a cavity surface 32 with a predetermined shape, and a support surface 34 around the periphery of the cavity. A preliminary structure is formed that includes a rigid base portion 35 (e.g., of polystyrene plastic) adapted to engage

the support surface 34 of the die 30, having inner and outer surfaces 36 and 37, and having an inlet passageway 38 and small air vents (not shown) communicating between its inner and outer surfaces 36 and 37. Also provided is a thermoplastic sheet 40 having a periphery 41 attached to the periphery of the base portion 35 with
5 the sheet 40 extending over the inner surface 36 to define a chamber 42 between the thermoplastic sheet 40 and the inner surface 36 of the base portion 35, which chamber 42 has a volume less than the volume of the cavity in the die 30 between the inner surface 36 and the cavity surface 32. The base portion 35 is positioned and may be clamped if necessary against the support surface 34 of the die 30 with
10 the thermoplastic sheet 40 positioned in the cavity at a position spaced from the cavity surface 32 (Figure 8). The molten gel is then injected by the extruder 10 through the inlet passageway 38 into the chamber 42 to thermally deform the sheet 40 into intimate engagement against the cavity surface 32 (Figure 9). When the gel has cooled there is formed a pad 44 including the 28 piece of solid elastomeric gel
15 having a surface very precisely corresponding in shape to the cavity surface 32 and overlaid by the sheet 40. The sheet 40 also corresponds very precisely to the cavity surface 32, has an inner surface coextensive with the top and side surfaces of said layer of gel, and is smooth and free of wrinkles.

The sheet 40 can be a laminate of an inner oil impervious thermoplastic
20 polymeric film and an outer conformable layer that provides a pleasing surface texture for contact by a persons hands and arms. As an example, a polyurethane blown microfiber web laminated to a polyurethane film has been found quite suitable. Such a laminate is described in U.S. Patent Application No. 08/490,464, filed June 14, 1995, Attorney Docket No. 51823USA9A.

25 The sheet 40 can be attached to the base portion 35 by heat sealing or other means, such as are described in U.S. Patent Applications Nos. 08/253,510 filed June 3, 1994, and 08/324,734 filed October 18, 1994.

While, as described above, molten gel can be fed directly from the extruder
10 into the chamber 42, solid elastomeric gel made using the extruder 10 or by a
30 batch process at an earlier time may be made molten and fed into the chamber 42 using means other than the extruder 10, such as by a melt pump (not shown).

Example 1:

Solid elastomeric gel has been produced by the following continuous extrusion process.

5 A copolymer commercially designated "Kraton (t.m.) 1107" and available from Shell Petroleum Company was introduced into a first infeed section 11a of the co-rotating twin screw extruder 10. The screw design of the extruder 10 was such that multiple mixing sections 12 each followed different multiple infeed sections 11 along the barrel 13 of the extruder 10. The copolymer introduced in the extruder 10 was heated and sheared in the first mixing section 12 immediately following its introduction into the first infeed section 11a. Mineral oil plasticizer similar to that described in U.S. Patent No. 3,676,387 was introduced at approximately a 1:1 ratio by weight with the copolymer at the second infeed section 11b of the extruder 10. Additional plasticizer was introduced at the third infeed section 11c at a ratio of 15 about 3:1 by weight with the copolymer, and still additional plasticizer introduced at the fourth infeed section at a ratio of about 4:1 by weight with the copolymer. The extruder 10 was fed with copolymer and plasticizer at a rate that produced 50 pounds per hour of the gel.

For purposes of comparison, solid elastomeric gel was also produced by the 20 following batch process.

A 75 gallon heated kettle was filled with the same ratio of the copolymer "Kraton (t.m.) 1107" and the mineral oil plasticizer described above to which was added a small amount of "Irgonox (t.m.) 1076 stabilizer. The mixture was agitated at medium shear for 8 hours.

25 The solid elastomeric gels produced by the above two processes were analyzed using gel permeation chromatography analysis ("gpc") to compare the percentages of tri-block and di-block copolymers in the gels, and thereby compare the amount of thermal and/or mechanical degradation the gels had undergone in their manufacturing processes (i.e., tri-block copolymers degrade to di-block 30 copolymers, so that the level of di-block copolymers in the gel is an indication of the amount of degradation that has occurred in the manufacturing process). The gel

made by the extrusion process contained 66.7 percent tri-block copolymers and 33.1 percent di-block copolymers, whereas the gel made by the batch process contained 52.7 percent tri-block copolymers and 47.3 percent di-block copolymers which indicated that significantly less thermal degradation had occurred in the
5 extrusion process than in the batch process.

The present invention has now been described with reference to one embodiment together with several modifications thereof. It will be apparent to those skilled in the art that many changes can be made in the embodiment and modifications described above without departing from the scope of the present
10 invention. Thus the scope of the present invention should not be limited to the methods and structures described in this application, but only by the methods and structures described by the language of the claims and the equivalents of those methods and structures.

Claims:

1. A method for making solid elastomeric gel from copolymer and plasticizer including the steps of:
 - 5 providing an extruder having multiple infeed sections each followed by a mixing sections along a barrel of the extruder;
operating the extruder while introducing the copolymer into one of the infeed sections of the extruder to heat and shear the copolymer in a subsequent mixing section;
 - 10 introducing the plasticizer to the copolymer through at least one of the feeding sections in a pattern and at a rate to produce solid elastomeric gel that at room temperature that will retain its shape after repeated compression and decompression cycles of the gel; and
ejecting the gel from the extruder.
- 15 2. A method according to claim 1 further comprising the steps of:
passing the gel through a die having a predetermined peripheral shape; and
cutting the extruded gel into lengths to form pieces of the gel with uniform cross sections that can be used in pads.
- 20 3. A method according to claim 1 further comprising the step of passing the gel through a die having a predetermined peripheral shape.
- 25 4. A method according to claim 1 further comprising the steps of:
providing a die having a cavity defined by a cavity surface with a predetermined shape and a support surface around the periphery of the cavity;
forming a preliminary structure including a rigid base portion adapted to engage the support surface of the die, having inner and outer surfaces, and having an inlet passageway communicating between said inner and outer surfaces; and a
30 thermoplastic sheet having a periphery attached to the periphery of the base portion with the sheet extending over said inner surface to define a chamber between the

thermoplastic sheet and the inner surface of the base portion, said chamber having a volume less than the volume of said cavity;

positioning the base portion against the support surface of the die with the thermoplastic sheet positioned in the cavity at a position spaced from the cavity surface; and

extruding the heated solid elastomeric gel through the inlet passageway into the chamber to thermally deform the sheet into intimate engagement against the cavity surface and to form, when the gel has cooled, a pad including a piece of solid elastomeric gel having a surface corresponding in shape to the die surface.

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5. A method for forming a pad comprising the steps of:

providing a die having a cavity defined by a cavity surface with a predetermined shape and a support surface around the periphery of the cavity;

forming a preliminary structure including a rigid base portion adapted to engage the support surface of the die, having inner and outer surfaces, and having an inlet passageway communicating between said inner and outer surfaces; and a thermoplastic sheet having a periphery attached to the periphery of the base portion with the sheet extending over the inner surface to define a chamber between the thermoplastic sheet and the inner surface of the base portion, which chamber has a volume less than the volume of said cavity;

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positioning the base portion against the support surface of the die with the thermoplastic sheet positioned in the cavity at a position spaced from the cavity surface;

heating solid elastomeric gel to a fluid state; and

injecting the heated solid elastomeric gel through the inlet passageway into the chamber to thermally deform the sheet into intimate engagement against the cavity surface and to form, when the gel has cooled, a pad including a piece of solid elastomeric gel having a surface corresponding in shape to the die surface between the deformed thermoplastic sheet and the base portion.

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6. A pad comprising a layer of solid elastomeric gel having top side and bottom surfaces, a rigid base portion having a periphery along said bottom surface, and a flexible oil impervious thermoplastic sheet having a periphery attached to the periphery of said base portion to form a chamber between said base portion and sheet, said sheet having an inner surface coextensive with the top and side surfaces of said layer of gel and being free of wrinkles.
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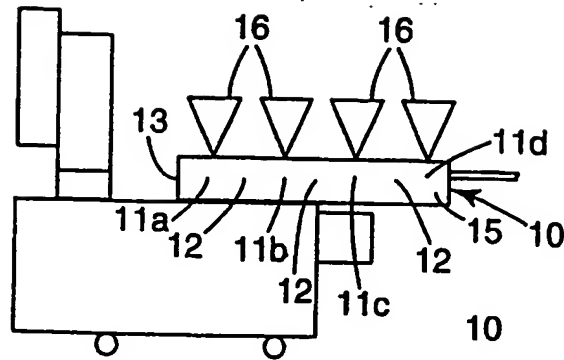


Fig. 1

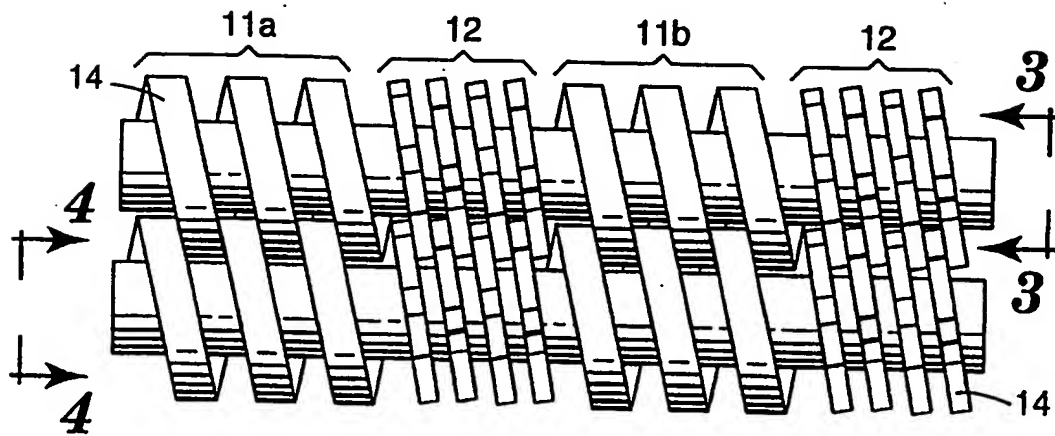


Fig. 2

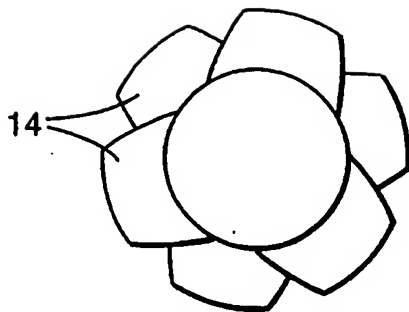


Fig. 3

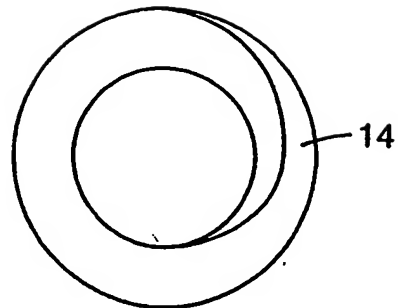
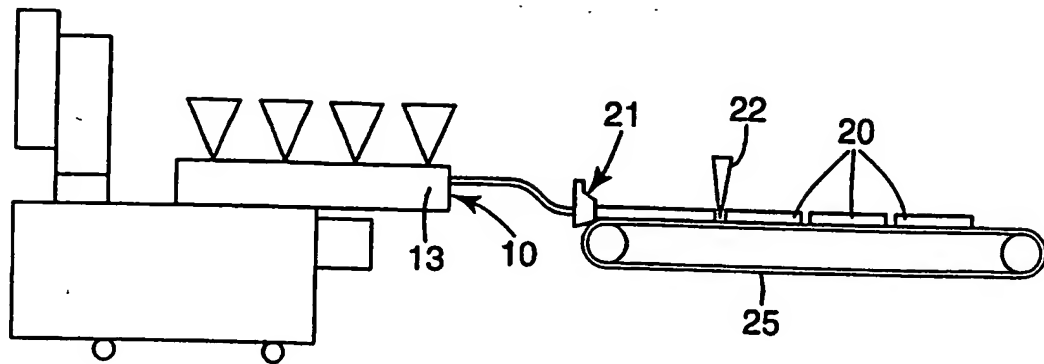
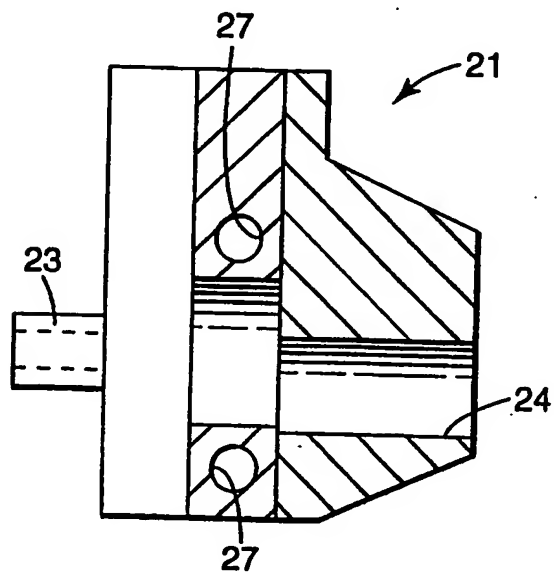


Fig. 4

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**Fig. 5****Fig. 6****Fig. 7**

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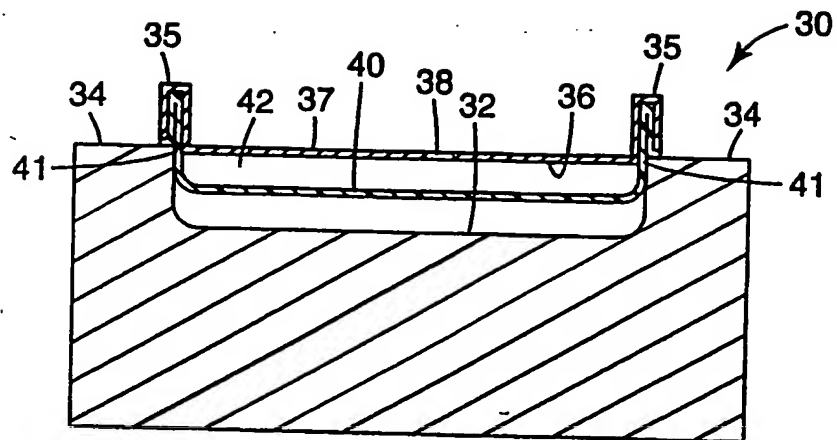


Fig. 8

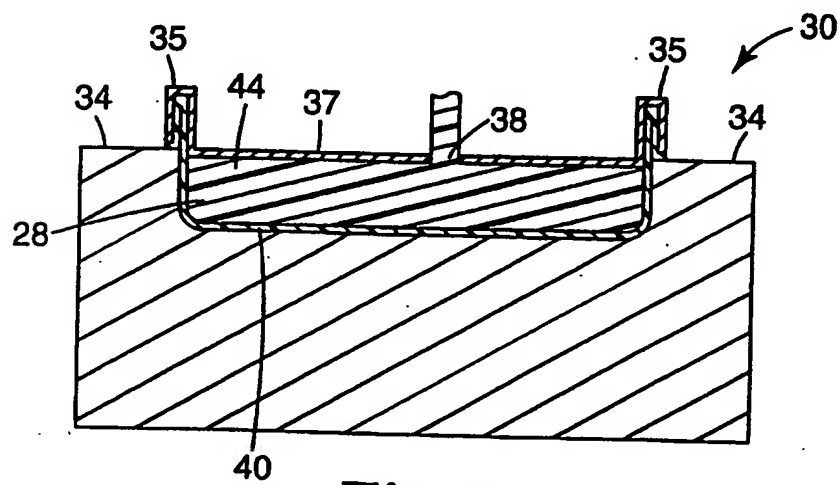


Fig. 9

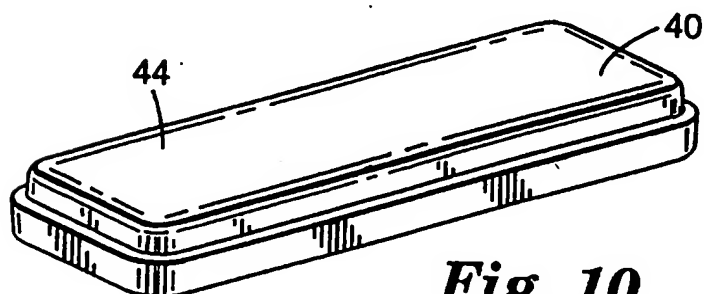


Fig. 10

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 96/06855

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B29C47/10 B29C43/18 B29C45/14 A61G7/057

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B29C A61G C08K C08L A47C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A,5 336 708 (JOHN Y. CHEN) 9 August 1994	1-3
A	see column 6, line 52 - column 7, line 18; claims 1,4-6; figure 2A	4-6
Y	US,A,3 814 563 (ROBERT K. SLABY ET AL) 4 June 1974	1-3
	see column 1, line 13 - line 24; claims 1-5; figure 1	
A	US,A,5 424 020 (TAKAHISA HARA ET AL) 13 June 1995	4
	see column 4, line 21 - line 41; figures 3A,7,8	
A	US,A,5 006 188 (MITSUJI USUI ET AL) 9 April 1991	4
	see claim 1; figures 1-9	
	-/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

10 September 1996

Date of mailing of the international search report

27.09.96

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE,A,17 04 943 (PRESSWERK KÖNGEN GMBH) 3 June 1971 see claim 1; figure 2 ---	5
A	PATENT ABSTRACTS OF JAPAN vol. 95, no. 002 & JP,A,07 032511 (ASAHI CORP), 3 February 1995, see abstract ---	5
A	US,A,4 788 730 (ROBERT A. BEXTON) 6 December 1988 see column 3, line 21 - column 4, line 6; claim 1; figure 3 ---	6
A	US,A,5 369 829 (ERIC C. JAY) 6 December 1994 see claim 1 ---	6
P,A	EP,A,0 702 917 (SANDEMAN ALLEN, NICHOLAS) 27 March 1996 see claim 1 ---	6
A	GB,A,1 202 301 (WERNER & PFLEIDERER KG) 12 August 1970 see page 2, line 29 - line 64; claims 1,3,5,7; figures 1-3 ---	1
P,A	EP,A,0 659 787 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 28 June 1995 see page 7, line 3 - line 11 ---	1
A	CH,A,536 655 (AWETA ANSTALT) 29 June 1973 see claim 1; figure 1 -----	1

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/US 96/06855

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-5336708	09-08-94	US-A- 4369284	18-01-83
		US-A- 5153254	06-10-92
		US-A- 4618213	21-10-86
		US-A- 5262468	16-11-93
		WO-A- 9600118	04-01-96
		US-A- 5508334	16-04-96
		US-A- 5475890	19-12-95
		US-A- 5324222	28-06-94
		US-A- 5239723	31-08-93
		US-A- 5334646	02-08-94
US-A-3814563	04-06-74	DE-A- 2145078	23-03-72
		FR-A- 2131214	10-11-72
		GB-A- 1359013	03-07-74
		NL-A- 7112242	23-03-72
US-A-5424020	13-06-95	JP-A- 3076614	02-04-91
		JP-A- 3261519	21-11-91
		CA-A- 2039160	22-02-91
		DE-D- 69021361	07-09-95
		DE-T- 69021361	29-02-96
		EP-A- 0439625	07-08-91
		ES-T- 2077684	01-12-95
		WO-A- 9102639	07-03-91
		US-A- 5275776	04-01-94
		EP-A- 0423676	24-04-91
US-A-5006188	09-04-91	JP-A- 1198314	09-08-89
DE-A-1704943	03-06-71	NONE	
US-A-4788730	06-12-88	CA-A- 1320595	20-07-93
		DE-A- 3881037	17-06-93
		DE-T- 3881037	05-01-94
		EP-A- 0349620	10-01-90
		JP-T- 2502344	02-08-90
		WO-A- 8905110	15-06-89
US-A-5369829	06-12-94	US-A- 5457833	17-10-95

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/US 96/06855

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-702917	27-03-96	GB-A- 2293320	27-03-96
GB-A-1202301	12-08-70	FR-A- 1570371	06-06-69
EP-A-659787	28-06-95	AU-A- 8161894	29-06-95
		BR-A- 9405195	01-08-95
		CA-A- 2138676	24-06-95
		CN-A- 1106418	09-08-95
		FI-A- 946002	24-06-95
		JP-A- 7206954	08-08-95
		NO-A- 944968	26-06-95
CH-A-536655	29-06-73	NONE	